

resistant version of the standard Zymark arm was chosen for this project. A special problem was posed, however, in the handling of these solutions in the volumes required (10–300 mL) without contaminating the delivery devices. A solution was found through the use of peristaltic pumps and three-way pinch valves. These components were assembled into a pump station controlled by digital signals from Zymark's Power and Event Controller [4]. Between test firings, the tygon tubing is replaced to avoid cross-contamination. In addition, the master solutions are shielded in a lead brick lined enclosure—the robot workcell is itself not enclosed.

The system that required the most extensive modification is currently enclosed in a stainless steel glovebox [5]. This application called for the transfer of samples of Pu-238 oxides into and out of calorimeters for measurement of their heat output. Pu-238 is an intense alpha emitter and, as an oxide, the particulate acquires a charge. These charged particles are very mobile, quickly contaminate any space, and even migrate into conductors shorting them eventually. All drive electronics were removed from the Zymark robot base and wrist, coatings were removed, and all plastic components were replaced with metal. The only components remaining with the robot arm are the servo motors and feedback potentiometers. Remoted electronics were placed in a separate housing and cabled to through the wall of the glovebox using special hermetically sealed feedthrough connectors.

Our experience with radiation environments, gloveboxes, and existing laboratories have led us to begin design of our own robotic arm. The system will be of a gantry geometry and be modular in the *x* and *y* dimensions in increments of 6 inches. This will allow us to size the robot to the existing work space and the intended application. The *z*-axis will be telescoping in on itself to limit the overall height of the robot. The gantry design permits maximum use of the bench space or glovebox floor for modules, while the robot itself uses previously unused space overhead. Laboratory remodelling costs will thus be circumvented. Additional specifications have been reviewed by many researchers and address such areas as material compatibility, precision, controller architecture, tool changing, etc. The arm will be compatible with other commercially available laboratory robotic modules (i.e., syringe stations, balances, centrifuges, etc.). We anticipate having prototypes available within 2 years.

References

- [1] Beugelsdijk, T. J., and Knobeloch, D. W., *J. Liq. Chrom.* **9**, 3093 (1986).
- [2] Beugelsdijk, T. J., Knobeloch, D. W., Thurston, A. A., Stalnaker, N. D., and Austin, L. R., Robot-Assisted Sample Preparation for Plutonium and Americium Radiochemical Analysis, in *Advances in Laboratory Automation-Robotics 1985*, Strimaitis, J. R., and Hawk, G. L., eds., 283.
- [3] Bowen, S. M., Beugelsdijk, T. J., and Knobeloch, G. W., Nevada Test Site Solution Dispensing Robotics System, in *Advances in Laboratory Automation-Robotics 1986*, Strimaitis, J. R., and Hawk, G. L., eds., 347.
- [4] Beugelsdijk, T. J., Bowen, S. M., Waters, D. S., and Schneider, D. N., A Non-Contact Pump Station for the Delivery of Radioactive Solutions, *Zymark Newsletter* **2**, 8 (1985).
- [5] Knobeloch, D. W., Austin, L. R., Latimer, T. W., and Schneider, D. N., Automation of the Calorimetry Step for Production of Plutonium-238 Oxide Fueled Milliwatt Generators, in *Advances in Laboratory Automation-Robotics 1985*, Strimaitis, J. R., and Hawk, G. L., eds., 313.

Microwave Acid Sample Decomposition for Elemental Analysis

H. M. Kingston and L. B. Jassie

Center for Analytical Chemistry
Inorganic Analytical Research Division
National Bureau of Standards
Gaithersburg, MD 20899

Appropriate sample preparation is essential to achieve both accuracy and precision in the analysis of materials. This preliminary step is one of the most time-consuming parts of many analyses and has become the rate limiting step for such multi-element techniques as ICP, XRF, and ICP-MS. Acid dissolution of biological and botanical samples can take from 4 to 48 hours using classical digestion techniques. Many of these same samples require only 10 to 15 minutes with microwave digestions, dramatically reducing preparation times. Volatile elements such as selenium, phosphorus, tellurium, and vanadium can be retained quantitatively in a sealed vessel using microwave decomposition prior to instrumental analysis [1]. The technique has been tested on all the major sample types including biological, botanical, geological, alloy, and glassy samples and has demonstrated advantages for each of these sample groups.

The development of real-time monitors for temperature and pressure in the microwave environment permits the investigation of closed vessel digestion using microwave energy as the heat source. It is necessary, however, to have an understanding of the fundamental concepts controlling interactions between microwave energy and the acid solution containing the sample.

Research has been conducted to identify these fundamental relationships and to develop methods that allow the analyst to predict, before programming and running the equipment, the conditions that will be generated during microwave digestion. This has been accomplished by measuring many of the parameters required to calculate the microwave power absorption by the mineral acids. Once the amount of energy that will be absorbed by a quantity of acid is determined, the equation is solved for the final temperature that will be reached by the sample at specific power settings. This method of predicting the temperature, or the time it takes to reach a particular temperature is useful in estimating the decomposition conditions [2].

This work has led to many new applications. Because microwave digestions occur in a well-defined, precisely controlled system, it is suitable for integration into automated applications. Acid digestion conditions have previously been too arbitrary for automation. With direct control of the power, the acid temperature, and the time for digestion, the microwave technique has become sufficiently structured so that it is possible to automate sample decomposition prior to instrumental analysis. New microwave-transparent vessels made of PFA Teflon and specifically engineered for this purpose permit the use of high temperatures (180–250 °C) and pressures (1000 kPa or 10 atm).

Because microwave energy is transferred directly to the acid, the reproducibility of decomposition conditions is better than can be achieved by traditional hotplate heating. Figure 1 shows the excellent reproducibility of sample conditions; it compares the temperature profile of two sets of six rice flour samples digested separately. The maximum difference between the sample temperatures at any point on the curve is 1.7%. Not only do the samples reach the same end point, but they achieve the same conditions at every point within this uncertainty.

Specific temperatures were identified for the rapid decomposition of the three basic components of biological and botanical matrices in nitric acid.

Carbohydrate matrices decompose rapidly at a temperature of 140 °C, protein molecules rapidly decompose at 150 °C, and lipid molecules decompose at approximately 160 °C. These temperatures were determined by observing the nitric acid decomposition of each of these biological components separately. Three carbohydrates were used (soluble starch, amylopectin-amylose and glucose). The proteins were modeled by using Albumin (SRM 926, a pure protein), and tristearin (C-18, fatty acid ester) was used for the lipids. The oxidation by nitric acid was determined by measuring a rapid rise in pressure inside the closed container during a small change in solution temperature.

Biological materials decompose rapidly at temperatures that are closely related to their major components. Because the biological matrix is converted to CO₂ and nitric acid is converted to NO₂, these gaseous decomposition products produce a sharp rise in pressure with barely perceptible temperature changes. This rise is a good indication of the occurrence of decomposition. Figures 2 and 3 show the increase in pressure with the increase in temperature for bovine liver compared to albumin and to tristearin. The decomposition of bovine liver resembles tristearin rather than albumin. Tristearin requires a higher temperature to oxidize in nitric acid than does albumin. It appears that the more acid-resistant component of the matrix may be left intact if the conditions are not vigorous enough. Even at conditions that decompose the carbohydrate, protein and fatty acid molecules, certain organic moieties, such as the nitrobenzoic acids, remain after treatment with nitric acid. The nitrobenzoic acids are formed by the nitration of the aromatic rings of certain amino acids and they do not degrade further [3].

An additional test to observe the completeness of the digestion with time was carried out by decomposing albumin. It was first digested for 10 minutes under normal conditions, then cooled to room temperature, and digested a second time. Figure 4 shows that the pressure versus temperature curves for the two tests are very different. The second decomposition curve resembles the partial pressure of pure nitric acid heated under these same conditions; this comparison is shown in figure 5. The fact that no additional pressure was developed during the second heating indicates that all the oxidation occurred in the first 10 minute exposure to nitric acid under these specific conditions of temperature and pressure. These results indicate that rapid oxidation of biological samples can be achieved in

approximately 10 minutes. The high temperature required for rapid oxidation of samples can be achieved reproducibly in a short period of time. These conditions require inert, closed vessels that can withstand substantial pressures and temperatures.

Because of the precise reproducibility of the conditions and decomposition, microwave dissolution has great potential as a tool in analytical laboratories. This new technique effectively addresses the problems of precision, accuracy and efficiency.

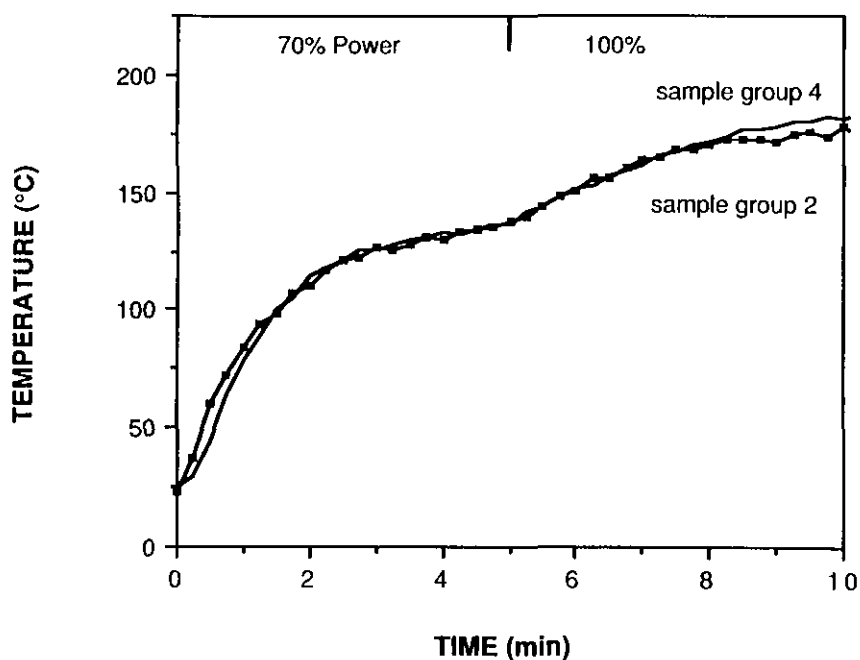


Figure 1. Temperature reproducibility of two sets of six samples each of 1 g of rice flour in 14 g of nitric acid.

Accuracy in Trace Analysis

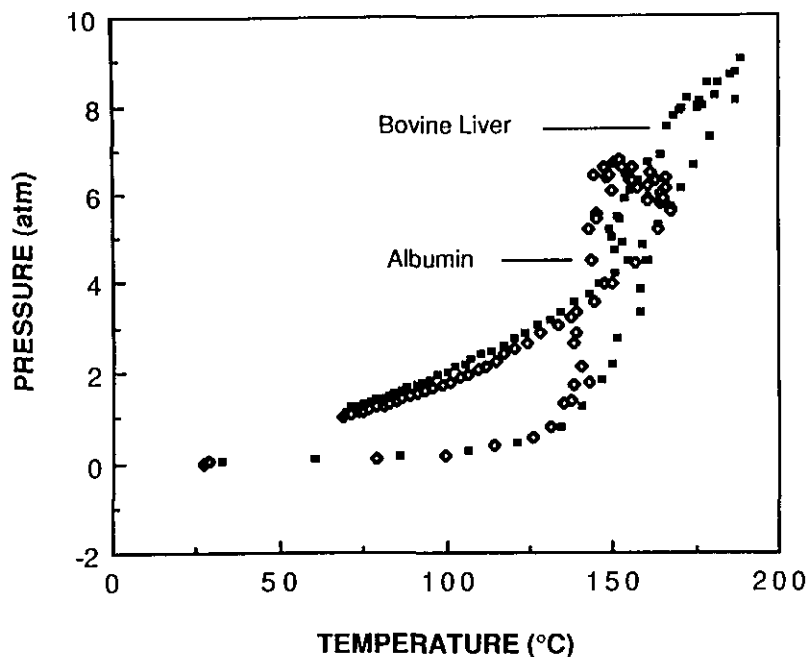


Figure 2. A comparison of the temperature versus pressure profile of acid decomposition of a biological tissue with that of a pure protein in the same acid.

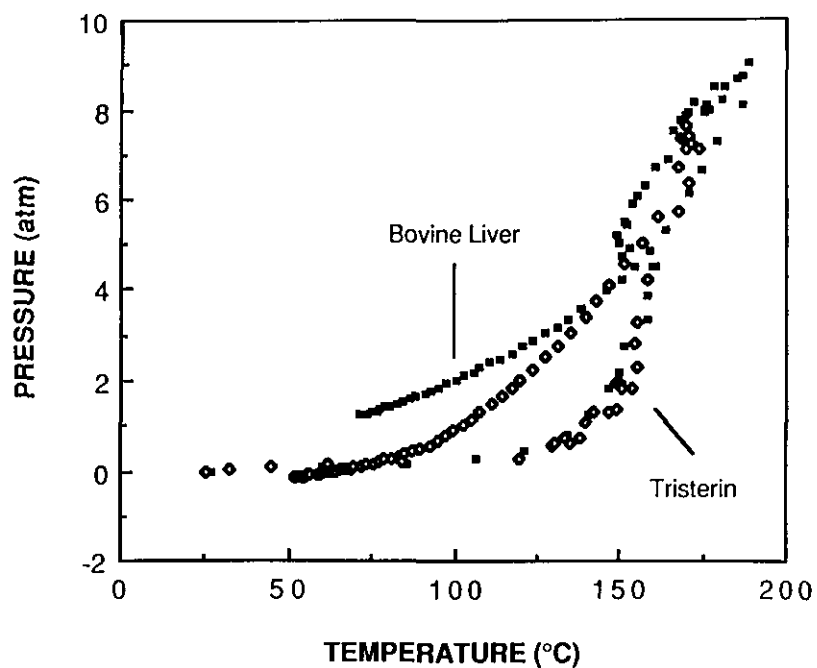


Figure 3. A comparison of the temperature versus pressure profile of acid decomposition of a biological tissue with that of a pure lipid.

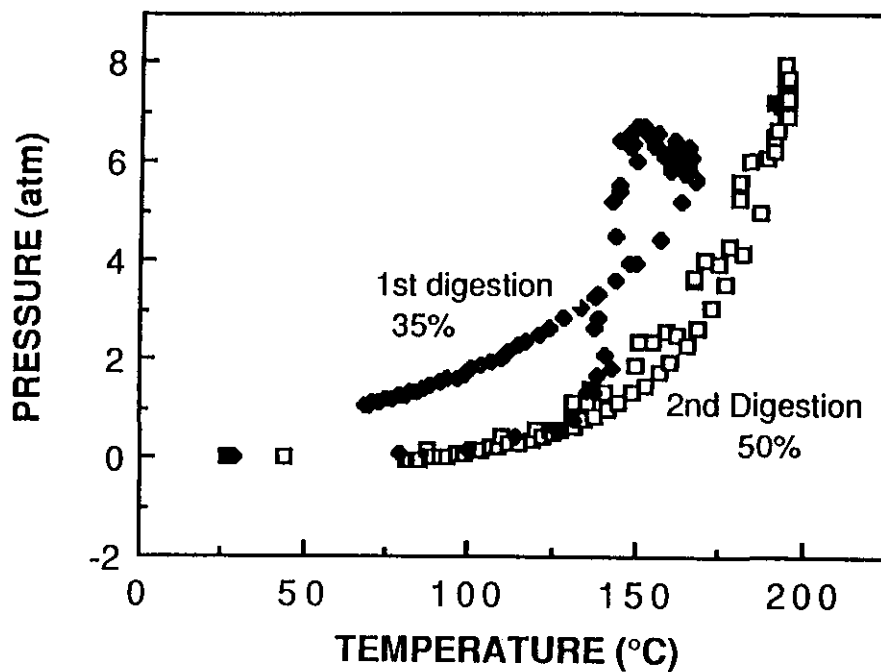


Figure 4. Temperature versus pressure profiles of the first and second digestions of a pure protein in nitric acid.

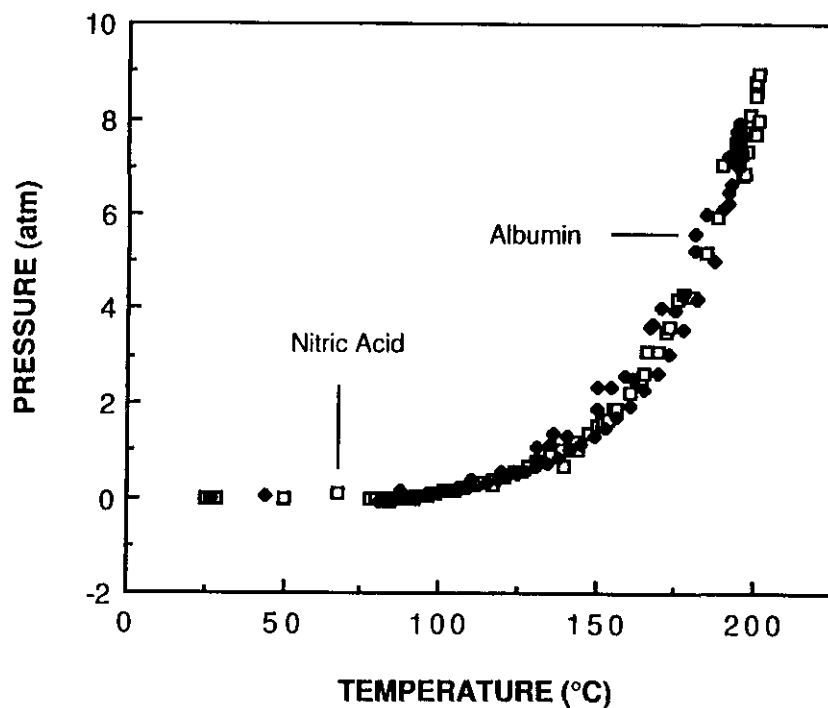


Figure 5. A comparison of the temperature versus pressure profile of the second digestion of a pure protein in nitric acid with that of nitric acid itself.

References

- [1] Paterson, K. Y., Veillon, C., and H. M. Kingston, "Microwave Digestion of Biological Samples for Selenium Analysis by Electrothermal Atomic Absorption Spectrometry" in *Introduction to Microwave Sample Preparation: Theory and Practice*, H. M. Kingston and L. B. Jassie, eds., ACS Reference Book Series, in press.
- [2] Kingston, H. M., and Jassie, L. B., *Anal. Chem.* **58**, 2534 (1986).
- [3] Pratt, K. W., Kingston, H. M., MacCrehen, W. A., and Koch, W. F., "Voltammetric and Liquid Chromatographic Identification of Organic Products of Microwave-Assisted Wet Ashing of Biological Samples" in press.

Solid Phase Extraction on a Small Scale

Gregor A. Junk and John J. Richard

Ames Laboratory (USDOE)
Iowa State University
Ames, IA 50011

1. Introduction

A wide range of sample size, flow rate, cartridge size, and volume of eluting solvent has been reported for the solid phase extraction (SPE) from water of a wide variety of organic compounds. Water sample volumes from 20–2000 mL, flow rates from 2–200 mL/min, cartridge sizes from 100–1200 mg, and volumes of eluting solvents from 0.1–5 mL have been used. At our laboratory, we have been able to achieve a concentration factor of 1000 and recoveries greater than 80% for pesticides [1] and tributyltin chloride [2] present at 0.1 ng/mL in water volumes of 100 mL. These results were obtained using 0.1 mL or less of ethylacetate to elute small cartridges containing 100 mg of C-18 bonded porous silica.

In this paper, we report the verification of this technique by extension to additional pesticides and polycyclic organic materials (POMs) and by field studies of surface and ground water samples where the SPE results are compared to those from conventional, accepted extraction procedures such as Amberlite XAD-2 [3] and solvent extraction.

2. Experimental

2.1 Extraction Procedures

2.1.1 Pesticides Cartridges containing 100 mg C-18 bonded porous silica, purchased from J. T. Baker (Phillipsburg, PA), were washed with about 3 mL of ethylacetate, followed by one column volume of methanol which was subsequently displaced with organic-free water. One hundred μ L of the standard pesticide spiking solution were added to 100 mL of water which was then forced through the cartridge, using a 50 mL glass syringe, at a flow rate of about 25 mL/min. The C-18 bonded porous silica was then dried by drawing room air through the cartridge using the vacuum from a water aspirator. The adsorbed pesticides were eluted by gravity flow of ethylacetate.

For on-site adsorption of the pesticides from collected surface water samples, the cartridges were preconditioned in the laboratory by washing with ethylacetate and methanol. The methanol was displaced with water and the cartridges were capped and transported to the sampling site where two 50 mL volumes of surface water were passed through each cartridge using a glass syringe. The cartridges were then returned to the laboratory for drying and elution. Duplicate water samples were collected in 4 L amber bottles and returned to the laboratory for processing using the XAD-2 procedure [3].

2.1.2 Polycyclic Aromatic Hydrocarbons (PAHs)

The PAHs were tested at 10 ng/mL using the same procedure used in the pesticide study. Recoveries were checked for partially dried cartridges using 100 μ L of benzene eluent. For field samples, solvent extraction with methylene chloride was used for comparison of recoveries with those obtained using C-18 bonded porous silica.

Standard capillary GC analyses were employed for the analyses of all eluates and extracts.

3. Results and Discussions

3.1 Pesticides

The recovery results from a previous study [1] and new results for some additional herbicides and insecticides are given in table 1.